Experimental Characterization of Methane Hydrate Bearing Sediments

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Project Personnel

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Collaborators:
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Dr. Roe-Hoan Yoon, Virginia Polytech Institute
Dr. SungPhil Kang, Korean Institute of Energy Research

Current Projects

1. **Relative Permeability Estimation** of Hydrate bearing Sands (collaboration with LBNL, current)

2. Observation of **Hydrate Formation Evolution** (collaboration with LBNL, current)

3. **Secondary Hydrate Formation** during Dissociation (current)

4. **Kinetic Study** on Methane Hydrate **Induction and Formation** (current)

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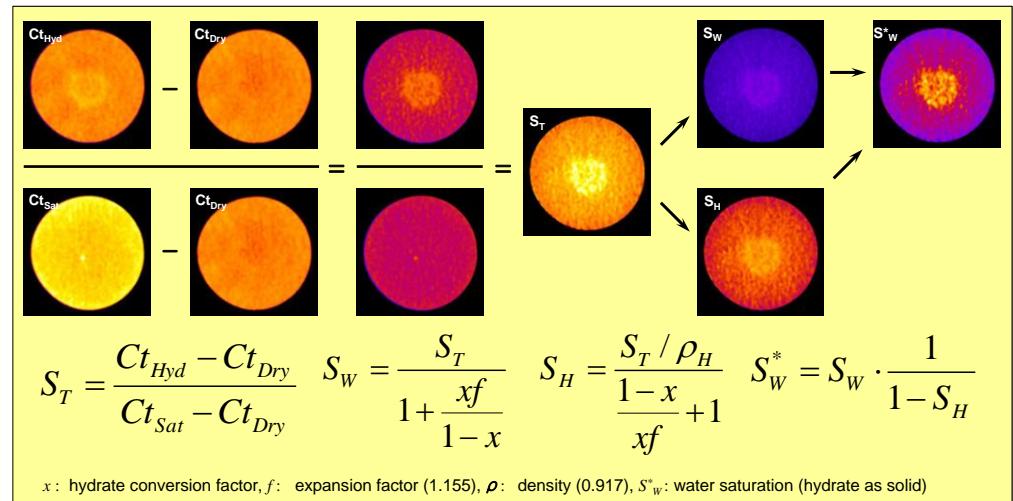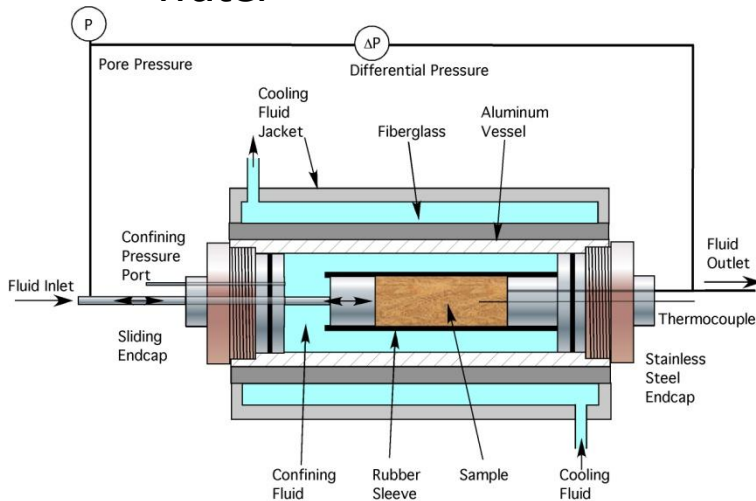4. Kinetic Study on Methane Hydrate Induction and Formation (current)

Relative Permeability Estimation

- **Steady state method** on lab-made hydrate bearing sands, using Darcy's equation and van Genuchten relative permeability relation:

$$k_r(s) = -\frac{Q(s)}{k_i \cdot \left(\dfrac{\rho g}{\mu}\right) \cdot A \cdot \left(\dfrac{dh}{dl}\right)} \qquad k_r(s) = \sqrt{S^*}\left[1 - (1 - S^{*1/m})^m\right]^2$$

- Measuring **permeability, differential pressure** during water flow
- **X-ray CT** used to measure **porosity, phase saturations** of hydrate and water

$$S_T = \frac{Ct_{Hyd} - Ct_{Dry}}{Ct_{Sat} - Ct_{Dry}} \qquad S_W = \frac{S_T}{1 + \dfrac{xf}{1-x}} \qquad S_H = \frac{S_T/\rho_H}{\dfrac{1-x}{xf} + 1} \qquad S_W^* = S_W \cdot \frac{1}{1 - S_H}$$

x: hydrate conversion factor, f: expansion factor (1.155), ρ: density (0.917), S^*_w: water saturation (hydrate as solid)

Relative Permeability Estimation

- The presence of hydrate in sands changes the relative permeability (k_r) and residual saturations, and the extent of changes were varied with the type of sands
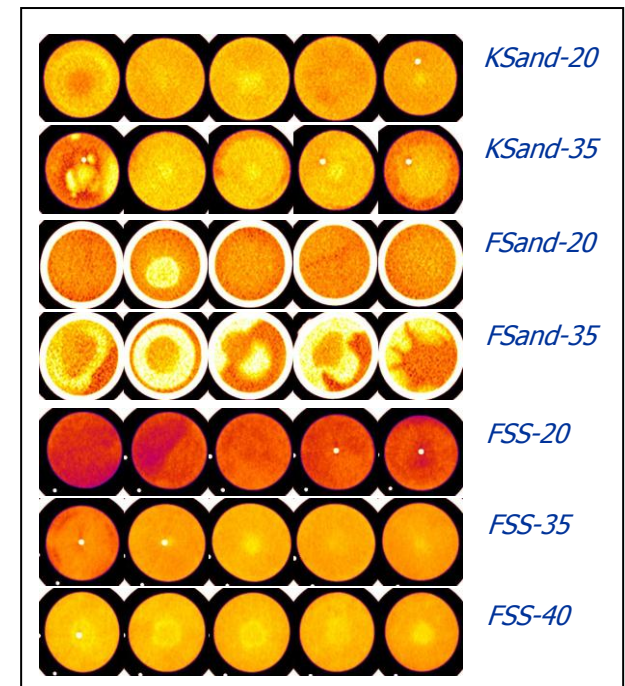
- Large ΔP (and k_r) variation on Ksand may be caused by irregular grain shape, and the k_r of Fsand (+silt) shows more consistency with hydrate saturations.

- The estimated parameters can be used for validation or prior information for transient-state relative permeability estimation method

KSand

FSand

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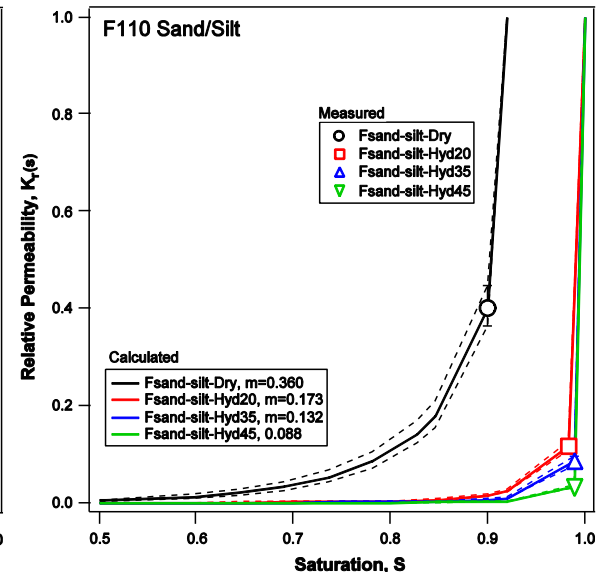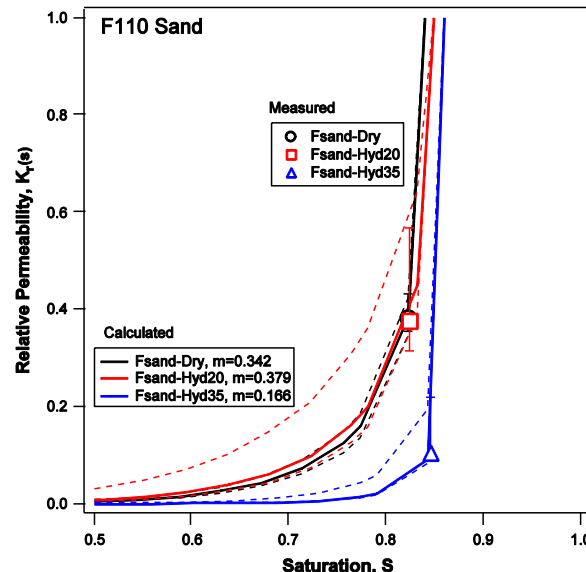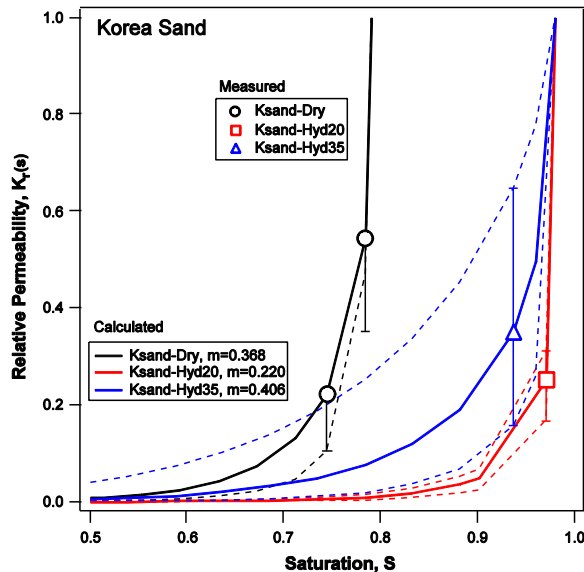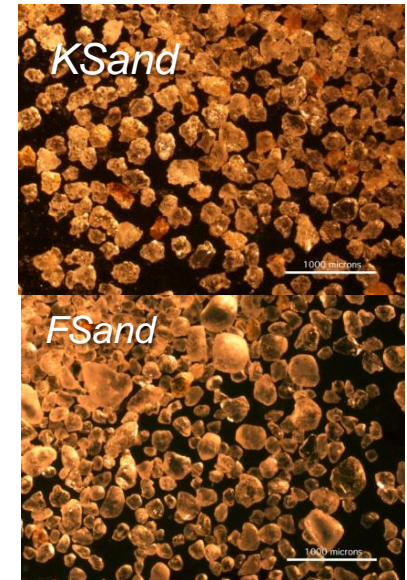
Future Work on Relative Permeability

- **Transient-state estimation** using CT measured phase saturation and results from the steady state method as a prior information for numerical inversion

  – Monitoring water saturation at certain locations and compare the water saturation with simulation results to find optimal parameter values of the selected constitutional relations

- **Heterogeneity** on the phase saturation and porosity will impact significantly

- Assumptions on homogeneous hydrate saturation distribution and porosity may not be reasonable for the core scale simulations.

- **CT images** can be used to provide the numerical simulation with **intrinsic heterogeneity on saturations and porosity**.
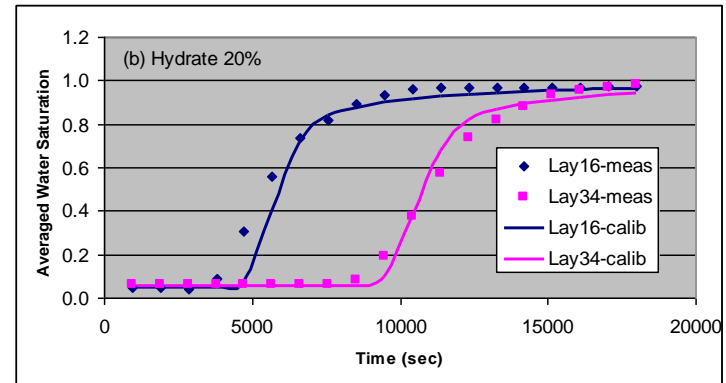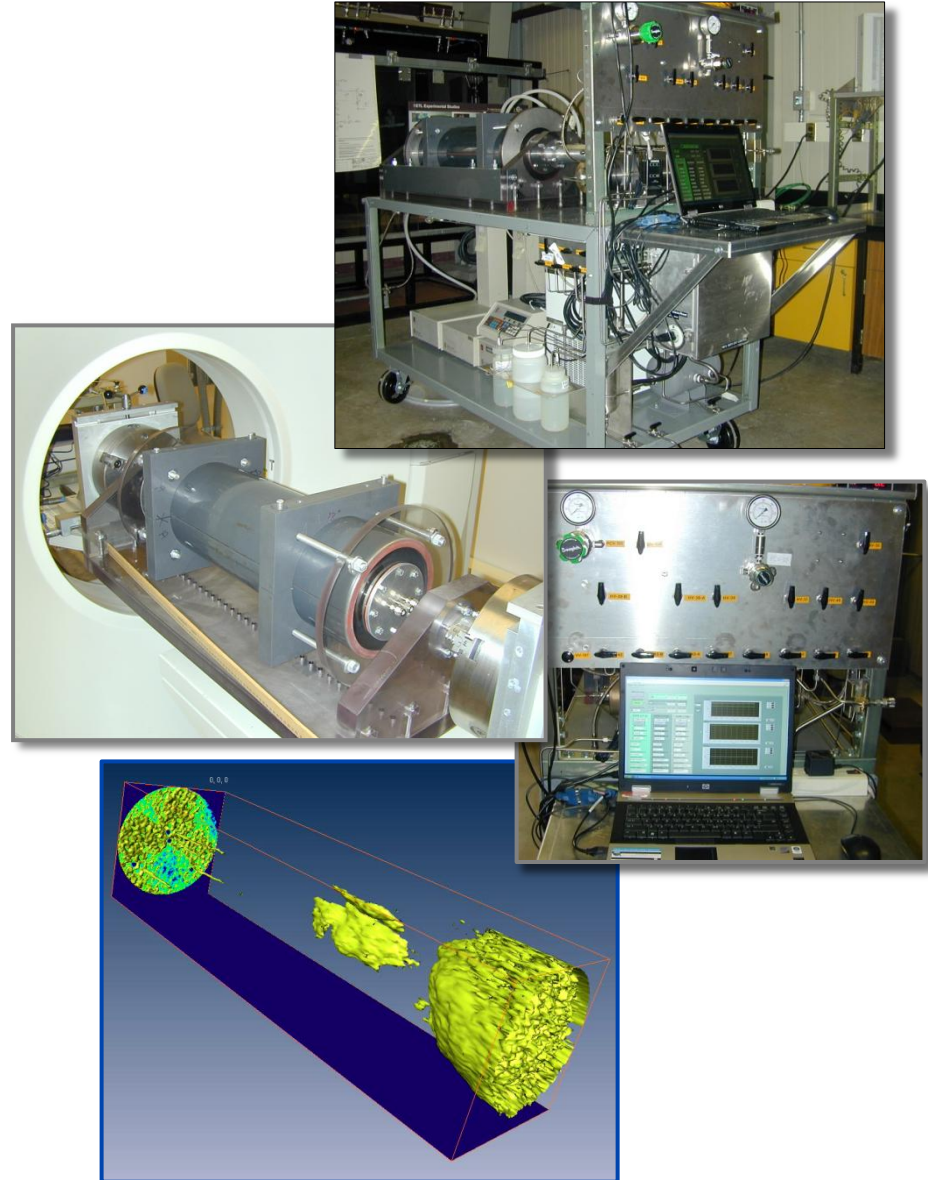

(b) Hydrate 20%

- Lay16-meas
- Lay34-meas
- Lay16-calib
- Lay34-calib

KSand-20
KSand-35
FSand-20
FSand-35
FSS-20
FSS-35
FSS-40

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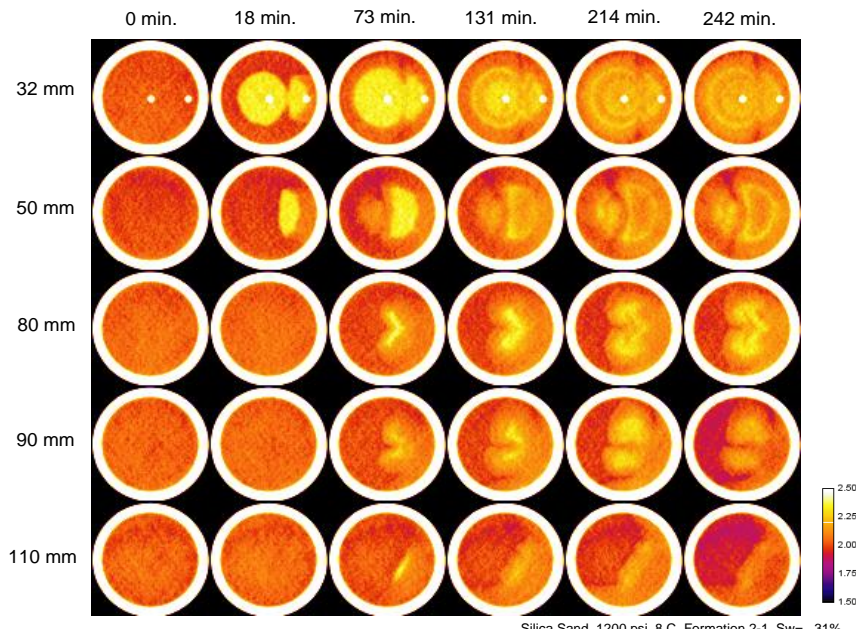
Hydrate Formation in Sands

- **Short term observations** (< 24 hr) of methane hydrate formation and reformation in F110 silica sand

- **Conditions:**
  - 1200 psi of pore pressure
  - 1500 psi of confining pressure
  - 8 °C of temperature (fixed)
  - 20 to 40% of initial water saturation
  - 40 % of porosity
  - Repetitive formations with varying time gaps (12 hr to 48 hr) between dissociation and consecutive reformation

- **Observations of hydrate distribution:**
  - Evolution of distribution patterns during a formation period (< 48 hr)
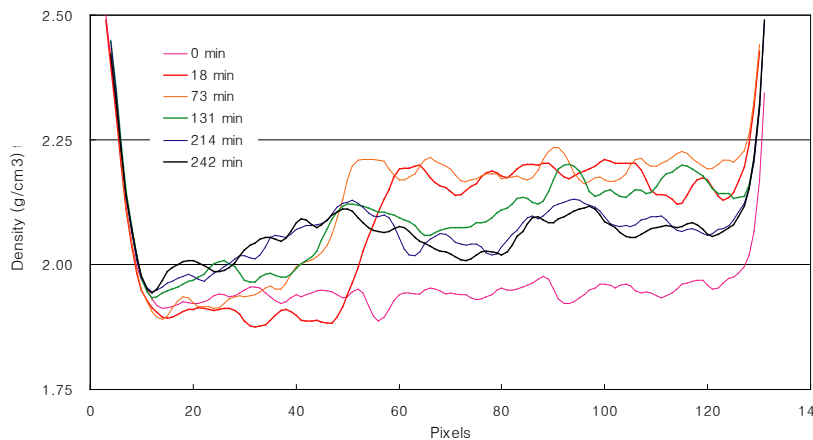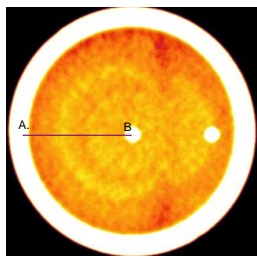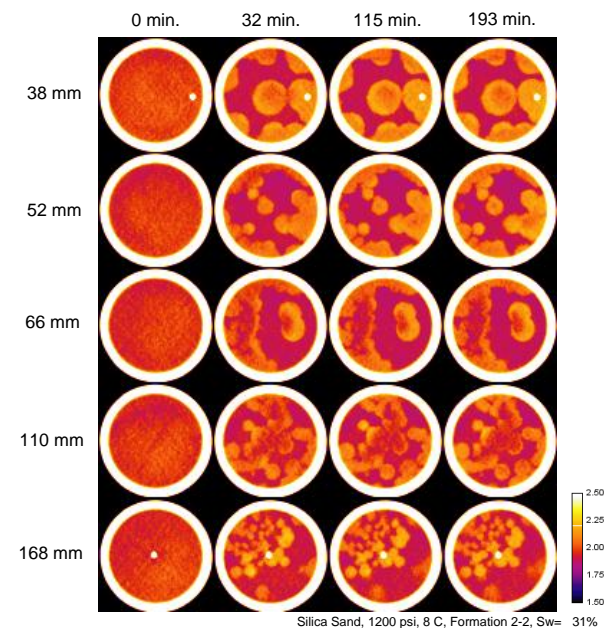 - Reproducibility of hydrate formation distribution at repetitive formations

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Short-Tem Hydrate Evolution

Wet sand with 31% of Sw

Silica Sand, 1200 psi, 8 C, Formation 2-1, Sw= 31%

Wet sand with 21% of Sw

Silica Sand, 1200 psi, 8 C, Formation 2-2, Sw= 31%


- Formation of hydrate with higher initial water saturation takes longer and shows evolving patterns.
- As hydrate forms, withdrawn water and accumulated hydrates increase density.
- Hydrate dissociation during formation is conjectured but not conformed.

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Repetitive Hydrate Formations

Silica Sand, 1200 psi, 8 C, Formation 5, Sw= 43%
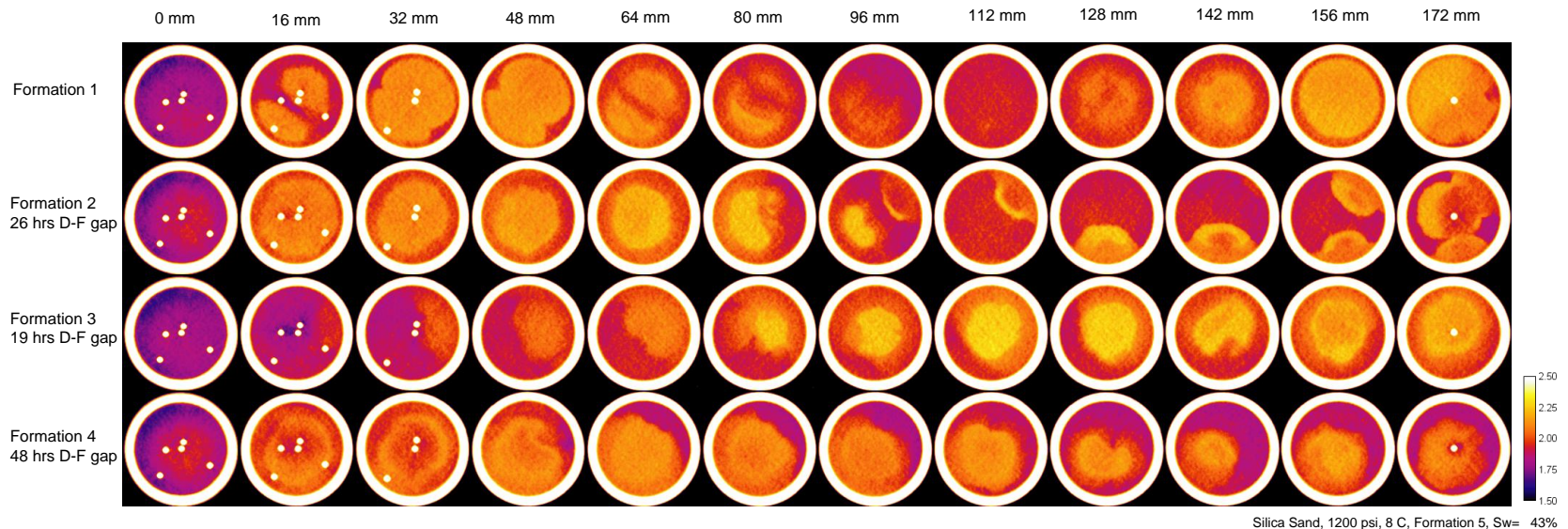
- Locations and saturation pattern of hydrate formation is **not reproducible and predictable**.

- Up to 48 hours of time gas between dissociation and reformation would **not impact on hydrate formation induction time**, at least in current PT condition (1200 psi and 8 °C)

- Hydrate formation renders water to move according to re-equilibrated capillary pressure field. Difference of density between dry and wet samples after hydrate dissociation shows the **redistribution of water**
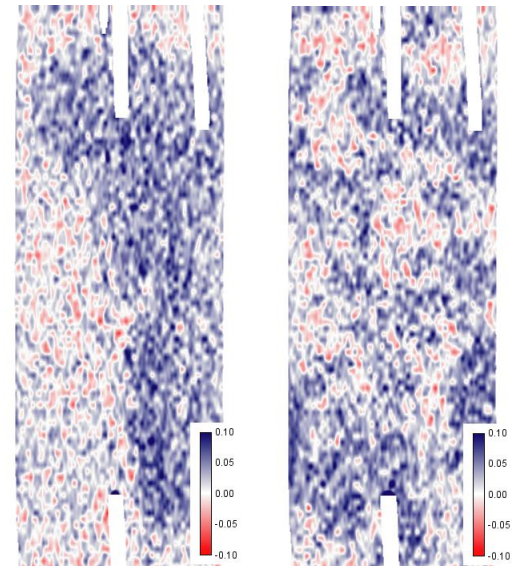
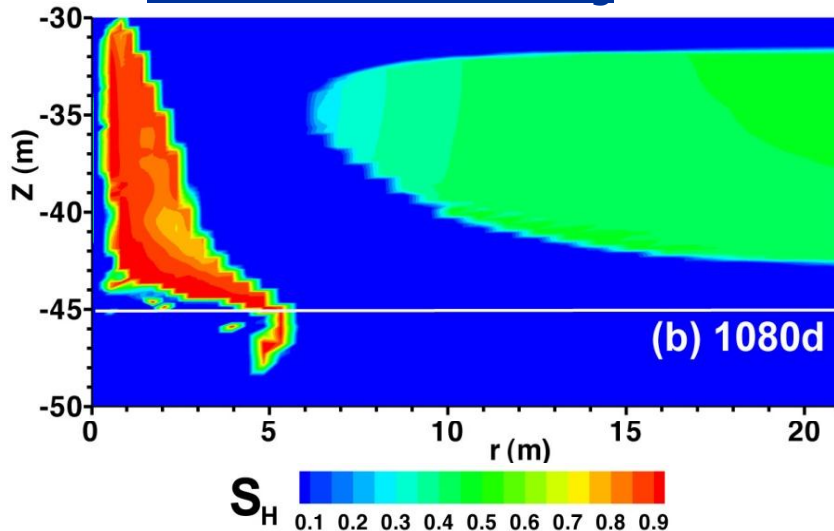**NATIONAL ENERGY TECHNOLOGY LABORATORY**

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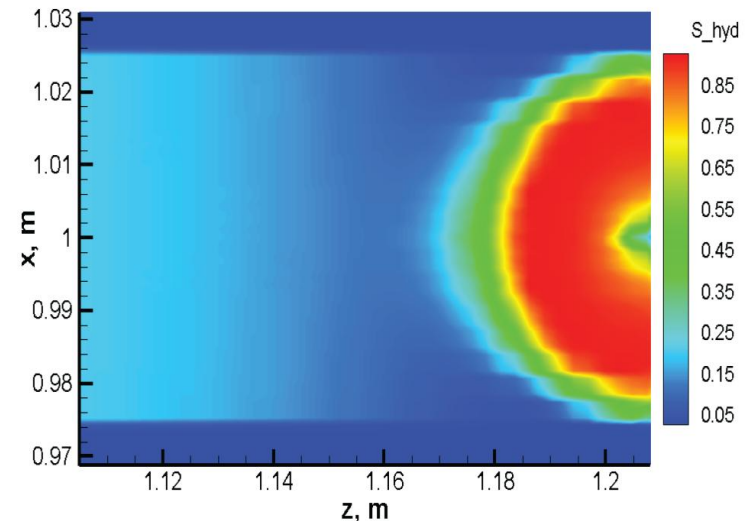4. Kinetic Study on Methane Hydrate Induction and Reformation (current)

Current Status of the Problem

- **Predicted secondary hydrate formation** during gas production in both reservoir and core scale
  - by lowered temperature (Joule-Thompson effect and endothermic nature of hydrate dissociation)
  - by elevated pressure (production shutoff and local heterogeneity)
  - by reduced salinity due to hydrate dissociation (core scale simulations)
- Additional treatments to inhibit hydrate formation have been recommended.
- **Experimental validation** of the hydrate formation is required.

- Reservoir Scale Modeling

(b) 1080d

S_H 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9

- Core Scale Modeling

S_hyd
0.85
0.75
0.65
0.55
0.45
0.35
0.25
0.15
0.05

Numerical Simulations

- **Core scale simulations using actual experimental conditions:**
  - sand core with 2" diameter x 5" length,
  - 35% porosity, 40% hydrate saturation,
  - saturated with saline water (3.5 wt%),
  - 1200 psi pore pressure, 8 °C temperature,
  - 700 psi pressure drop for depressurization,
  - heat flow allowed or adiabatic
- **Secondary hydrate formation occurred**
  - Adiabatic condition with saline water,
  - When Heat flow allowed only through a exiting port
- **Secondary hydrate formation NOT occurred**
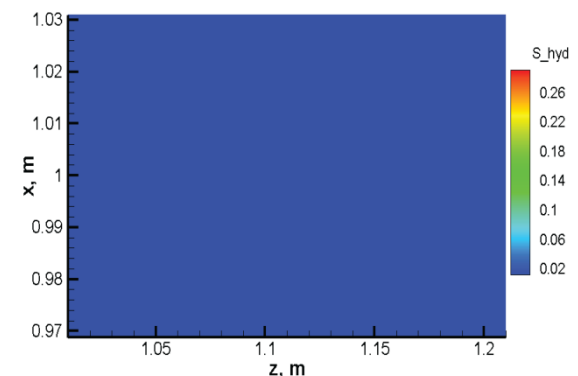 - When heat flow is allowed through side boundary (rubber sleeve)

Adiabatic
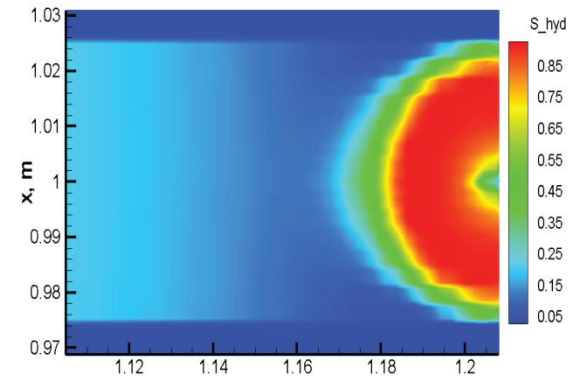
Point Heat Flow
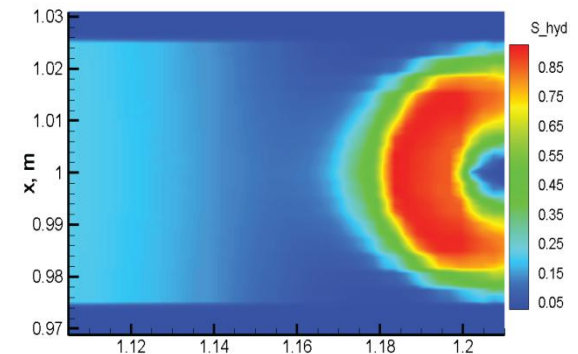
Side Heat Flow

Experiments

- **Experiment procedure:**
  - Wet sand uniformly packed (2" d x 5" l., 35% Porosity),
  - Methane hydrate formed (40% Sh),
  - 1200 psi pore pressure, 8 °C temperature,
  - saturated with saline water (3.5 wt% KI),
  - 700 psi pressure drop for depressurization,
  - heat flow allowed through rubber sleeve
  - temperature lowered in confining fluid prior to depressurization to mimic adiabatic condition

- **Heterogeneity in hydrate saturation was observed.**

Porosity
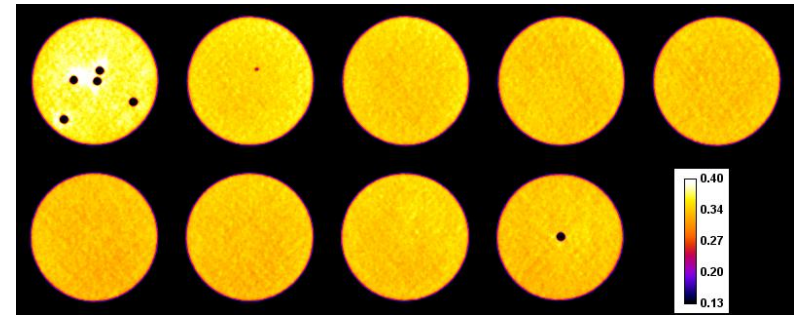
Hydrate Saturation
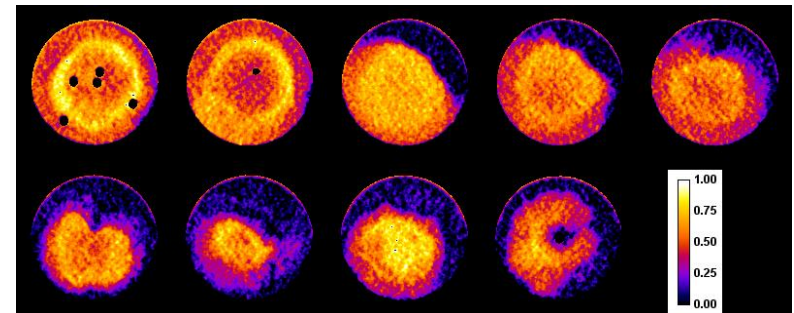
Water Flooded (Density)

Experiment Results

- Secondary hydrate formations (higher density) are **NOT observed in ALL cases**.

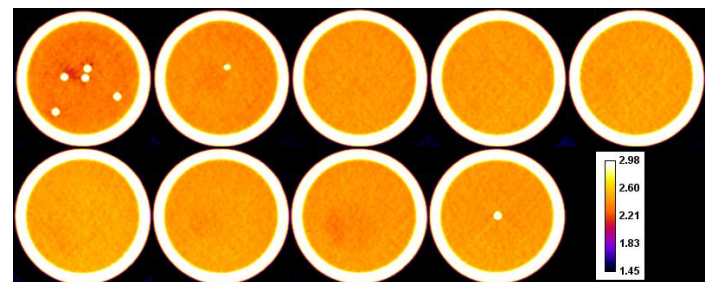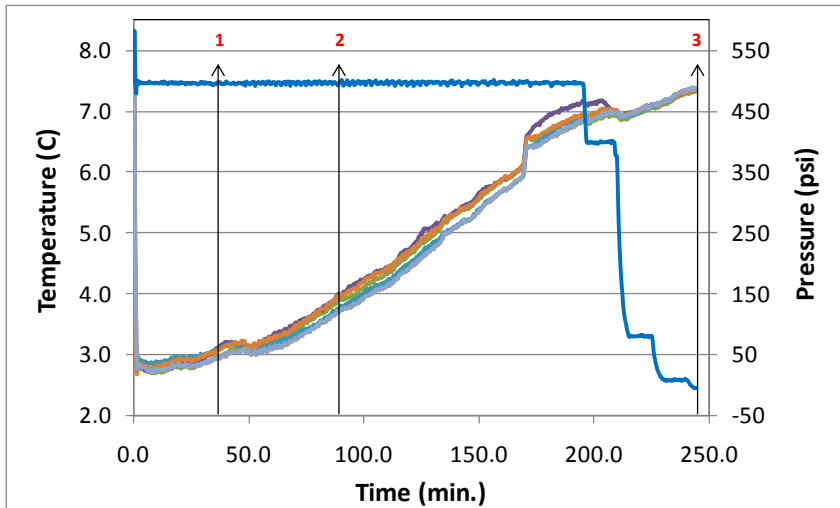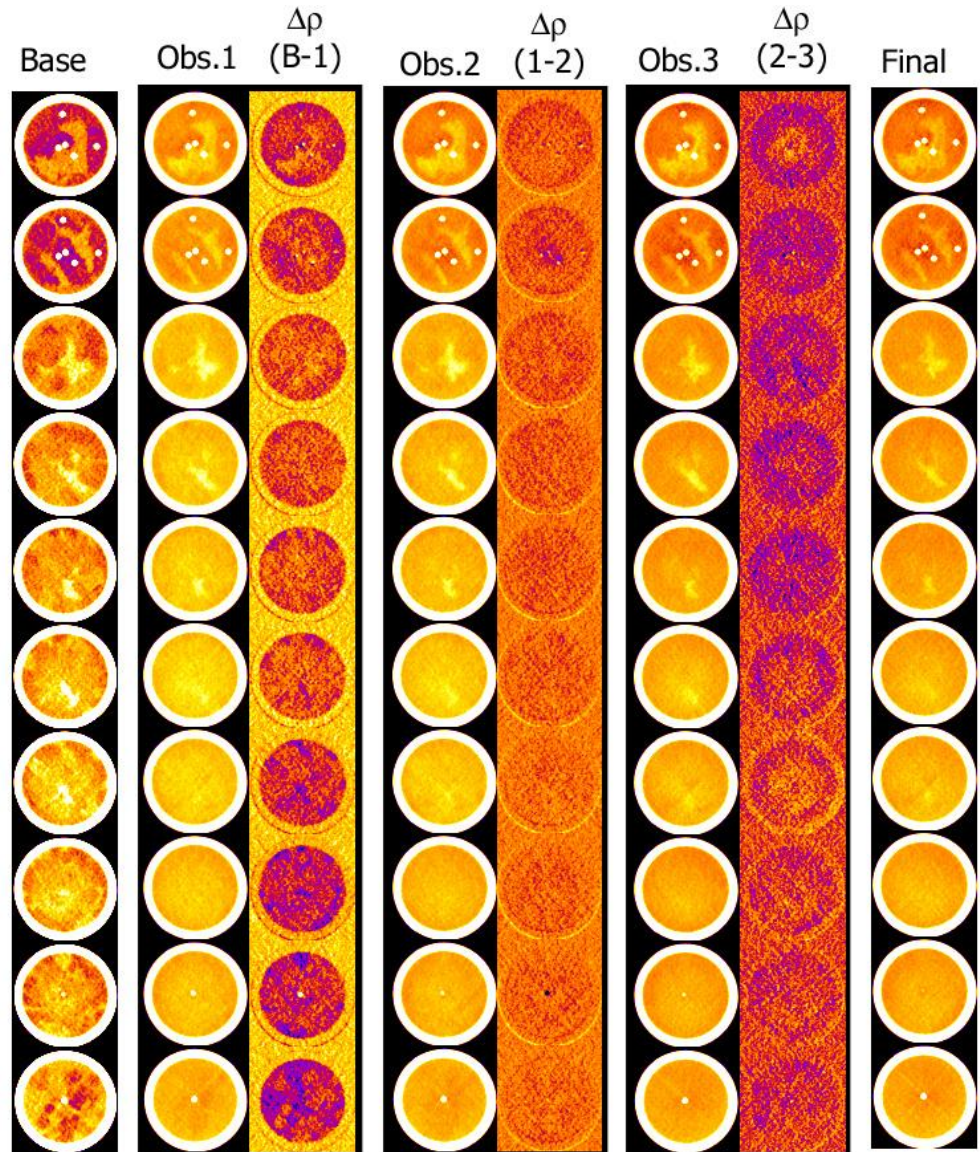- Potential **preferential pathways** (dark spots) of fluid were observed during dissociation.

- **Non-uniformity in fluid flow** and **uneven salinity reduction** may result in absence of formation.

Converting CT images into Numerical Mesh

- Image on each slice of CT scan from medical CT have **512x512** pixels and 100 images on a stack for a core sample, that is **26 million pixels**!

- Need to **simplify the image** by setting specific grids that are homogeneous within the grid but **preserves the heterogeneous entirety** of each image.

- The processed images then can be **converted into an input file** for numerical simulators such as **FLEUNT** and **TOUGH2**.

- Developed **an automated tool** that can generate reduced CT images, using MATLAB and ImageJ (NIH).

- Total pixel number can be reduced to less than **100 thousands**.
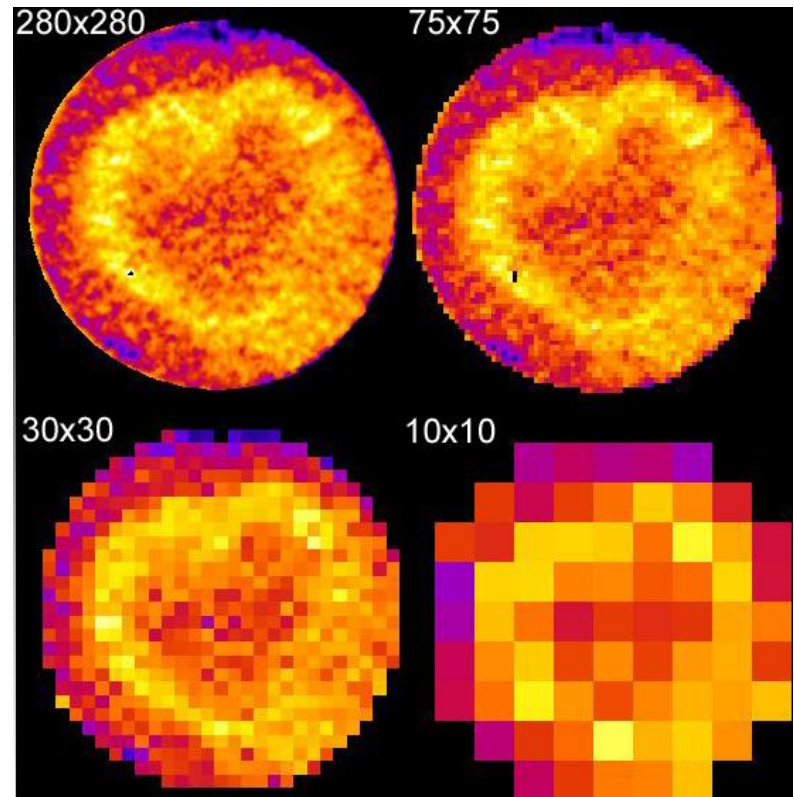
Future Work

- **Advanced core scale simulations with measured permeability, porosity, and hydrate saturation**
- **Mesh for input to simulators with intrinsic heterogeneity derived from X-ray CT images**
- **Potential applications of the conversion:**
  - All core scale simulations (relative permeability test, hot water injection test, secondary hydrate formation test, etc)
  - Heterogeneity upscaling to reservoir scale statistically
  - Natural samples into numerical simulations

280x280x94 → 7.4 million pixels
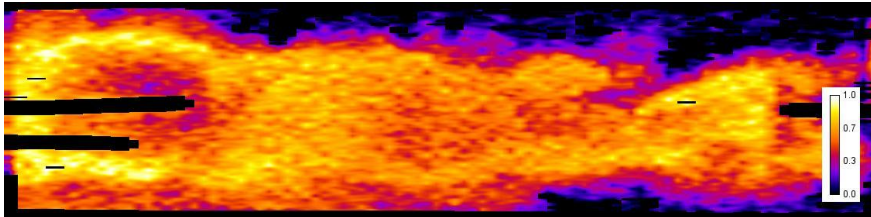
30x30x94 → 85 thousand pixels
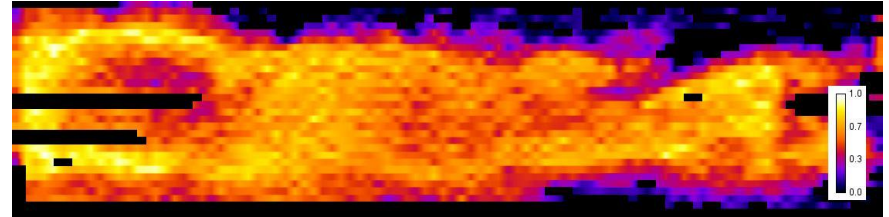
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Kinetics of Hydrate Formation

- **Background**
  - Hydrate reformation was predicted by numerical simulation during gas production
  - Availability of kinetic data on hydrate formation is limited or dissociation kinetic data are used for formation as well.
  - Develop equipment and procedures to reliably and reproducibly form methane hydrate and measure <u>hydrate formation induction time and gas consumption rates</u> in various porous media of interest
- **Expected impacts**
  - Provide information useful for
    - Developing reliable kinetic models to be applied for numerical simulations of hydrate production
    - Predicting potential impacts of hydrate formation kinetics on production strategies for hydrates
    - Contributing to identify optimal models of hydrate formation for production simulation

Approaches

Developing gas hydrate system in porous medium

- **Static system** (no vortex): Diffusion dominated gas transfer for hydrate formation results in slower formation of hydrate.

- **Sediment surface**: Greater interface area between gas and liquid enhances hydrate formation.

- Unlimited or limited methane gas supply for P/T observation

- **Multiple pressure vessels** to reproduce abundant data for statistical analysis

- **Smaller volume** of aluminum vessel with high thermal conductivity

Multi-Pressure Vessel System (MPV)

SECTION A-A

Hydrate Formation Induction

natural silica sand system — T1, T2, T3

hydrophobic sand system — T1, T2, T3, T4
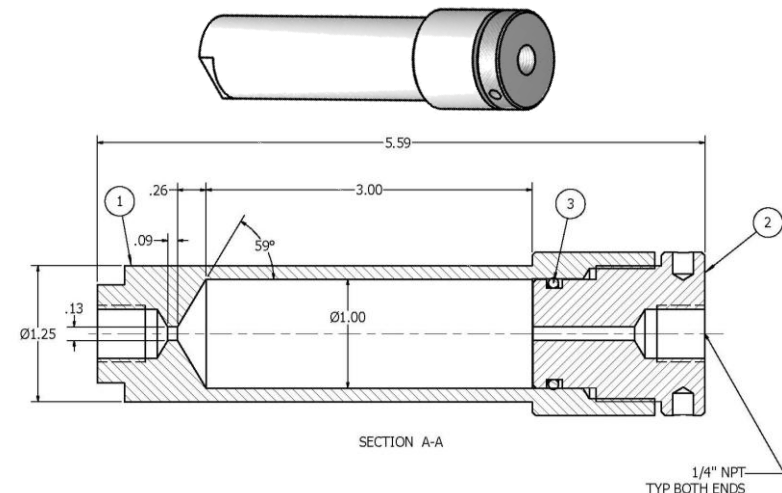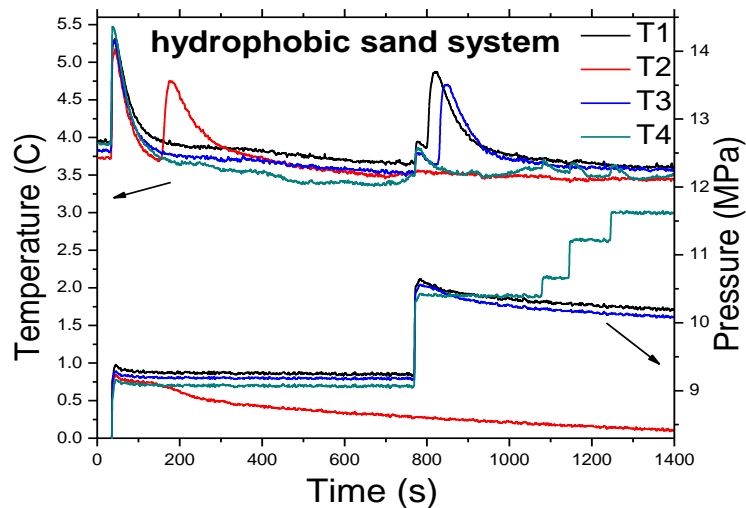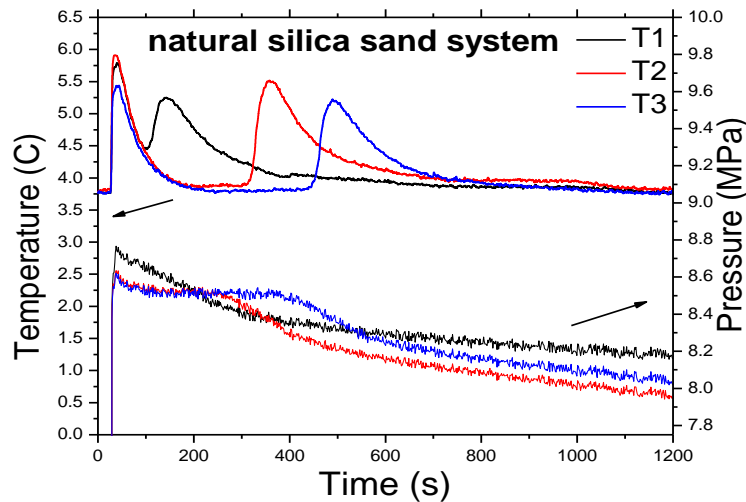
Formation Condition:
- Constant temperature: 3.8°C
- Initial pressure: 8.7 ~ 11 Mpa
- Water saturation: ~80%
- Materials:
  - (a) natural silica sand (~ 150μm),
  - (b) surface modified hydrophobic silica sand (~ 150μm, contact angle 20°)

Observations:
- Hydrophobic sand system required higher driving force for hydrate formation
- Sand surface hydrophobicity introduced difficulty and randomness to gas hydrate formation

Technical Challenges

- **Probabilistic nature of hydrate inductions**
- **Numerous key parameters:**
  - Porous Medium
  - Driving Forces
  - Thermal History of Waters
- **Separation of formation kinetics from heat and fluid conductivity**
  - Independent measurements for thermal conductivity and relative permeability of fluids are necessary
- **Discrepancy between natural and synthesized hydrates**
  - Hydrate occurrences (i.e. pore filling, cementing, or filming)
  - Phase saturations (water-gas system vs. dissolved gas system)
  - Heterogeneity in natural sediments: grain size distribution, surface roughness, compactness, etc.

Future Steps

- **Apply CT scanning technique** to monitor CT image of hydrate formation at real time

Cooling Fluid   Plastic Water Jacket   Thermo couples   Gas
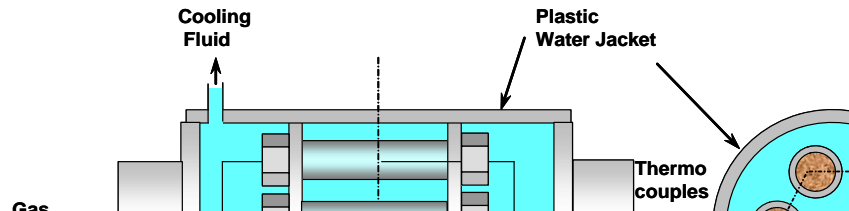
- Investigate the effect of **driving force** by choosing different formation P/T conditions within hydrate stable zone

- Systematical tests for the effect of **various degrees of surface hydrophobicity** on hydrate formation kinetics

- Study the effect of **sand particle size** by introducing **various materials** (e.g. clay, silt etc.)

- Modify/develop **empirical equations** for gas hydrate formation kinetics

- **Collaboration** with **Dr. Roa-Hoan Yoon** in Virginia Tech

Current/Proposed Projects

1. Observation of Gas Migration and Hydrate Formation in Saturated Porous Media (current)

2. Measurement of Geomechanical and Acoustic Properties of Synthesized Hydrate-Bearing Sediments (current and proposed)

3. Thermal Property Measurements (current and proposed)

4. Micro Imaging Hydrate Experiments (proposed)

capillary pressure

fracture opening

Fluid Outlet

Moving Stainless-Steel End Cap

Confining Fluid Inlet

Confining/Cooling Fluid

Confining/Cooling Fluid Port

Core

X-Ray

Rubber Sleeve

Confining/Cooling Fluid Port

Aluminum Confining Vessel

Fixed Stainless-Steel Endcap

Fluid/Thermocouple Inlet

CH 5

(b) Fine Grained

(e)

(f)

GAS

GAS

GAS

Sample Material

PVC

Sensor can be placed against core surface

*Jain and Juanes (2008), Behseresht *et al.* (2008 a, b)